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Instrument-Independent MS/MS Database for XQQ Instruments: A Kinetics-Based Measurement Protocol

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A detailed kinetics-based measurement protocol is proposed for the development of a standardized MS/MS database for XQQ tandem mass spectrometers. The technical basis for the protocol is summarized. A CAD database format is proposed.

Key words: CAD; CBRIS; characteristic branching ratios of ionic substructures; collisionally-activated dissociation; database; ion-molecule kinetics; measurement protocol; MS/MS; NIST-EPA International Round Robin; spectral library; standardization; tandem mass spectrometers; XQQ instruments (QQQ, BEQQ, etc.).

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1. Introduction

Tandem mass spectrometry (MS/MS) is widely used for structure elucidation and for the analysis of multicomponent mixtures [1]. The analysis makes use of the collisionally-activated dissociation (CAD) of "parent" ions. A parent ion may be a molecular radical cation, a protonated molecule, or a "progeny" fragment ion (daughter, granddaughter, etc. produced by the fragmentation of a larger precursor parent ion). The MS/MS technique consists of three steps: (i) a parent ion is mass selected by the first mass analyzer (designated MS-I); (ii) the selected parent ion collides with a target gas which is located within a reaction region between MS-I and the second mass analyzer (designated MS-II); and (iii) the undissociated parent ions and the progeny fragment ions which were produced within the reaction region are channeled into MS-II for mass analysis. MS/MS instruments thus produce a CAD spectrum of each initially-selected parent ion.

Reference [1] provides an excellent up-to-date review of the capabilities and advantages of the MS/MS technique. Among the advantages enumerated in [1] for MS/MS are:

(a) the functional group specificity of neutral loss experiments (for which there is no analogue in GC/MS) provides the unique ability to rapidly screen unknown mixtures for compound classes (e.g., nitroaromatic cations can be inferred by their loss of NO).

(b) the ability to perform very rapid analyses of targeted compounds in complex mixtures based on unique progeny ions (especially when "soft" ionization techniques are used) or on neutral loss experiments [e.g., the nitroaromatics screened above in (a)], thus avoiding the need to identify every component.

(c) very low limits of detection ($\leqslant$ppt; better than a single stage of mass spectrometry) can be attained with enhanced signal/noise ratios be-

cause of the elimination of "chemical noise" [1].

(d) unstable or extremely reactive species, which cannot be studied directly by optical spectroscopies, NMR, or GC/MS, have been studied directly by MS/MS (e.g., radical trapping of polyatomic free radicals; neutralization-reionization mass spectrometry [1]; etc.).

In principle, standard CAD spectra of a variety of ions (fragment ions, molecular ions, protonated molecules, etc.) could be generated and collected as reference libraries, to be used for comparison against unknown spectra in a manner analogous to the use of reference libraries in the data handling systems of ordinary electron impact mass spectrometers. Further, it should be possible to infer the identity of an unknown molecule by identifying the ionic substructures of fragment ions generated in its CAD spectrum. However, to date reference libraries of CAD spectra have not been collected because of a lack of standardization of operating conditions of MS/MS instruments [1].

This paper addresses the standardization of one of the major classes of commercially-available analytical MS/MS instruments, the so-called "XQQ" tandem mass spectrometers (there are currently more than 400 XQQ MS/MS instruments worldwide, representing a capital investment in excess of $170 million). XQQ instruments have three components: X1 Q2 Q3. X1 designates the first mass analyzer, which can be a quadrupole mass filter (represented by a Q), a reversed-geometry magnetic/electrostatic sector instrument (represented by BE), etc. Q2 designates a quadrupole mass filter operated with only radiofrequency (rf) potentials [no direct current (dc) potentials are used]. Q2 contains the target gas, and provides efficient ion containment of parent ions and of progeny fragment ions. Q3 stands for the second mass analyzer, a quadrupole mass filter.

Because XQQ instruments (QQQ, BEQQ hybrid, etc.) are complex ion-optical devices [2]–[9], the observed spectra can be extremely dependent on the experimental parameters used during the analysis. That is, one observes instrument-dependent CAD spectra. This was clearly demonstrated in a 1983 international round robin [10] wherein very different CAD spectra were observed for the same molecule. That is, the relative intensities measured in different QQQ instruments for any given pair of progeny ions differed by factors ranging into the hundreds, even though the same *nominal* operating conditions were supposedly used in each of the QQQ instruments. Therefore, until now it has not been possible to use a CAD spectrum of a given species in one XQQ instrument to identify and quantitate that same species in a different XQQ instrument.

To develop an instrument-independent MS/MS database (or library) for XQQ instruments, instrument users must be able to tune their instruments to obtain undistorted, dynamically-correct (i.e., instrument-independent) representations of any reactions studied within such instruments [9]. That is, the measurements must be substantially free from kinetic interferences (viz., every effort must be made to ensure a well-defined gas target and to prevent back reactions, impurity reactions, scattering losses, fringing fields, mass discrimination, etc.). The branching-ratio measurements must be precise and accurate (±10%).

Recent work from this laboratory has explored the prerequisite conditions for obtaining instrument-independent dynamically-correct branching ratios for the CAD of ions within XQQ instruments [9]. In this paper a kinetics-based measurement protocol is described for the determination of standard CAD spectra within XQQ instruments. The technical basis for the protocol is summarized. Table 1 includes a typical CAD spectrum measured using this protocol.

This protocol can also be used for the development of a standardized MS/MS database for XQQ instruments. One of the goals of this paper is to promote discussion about the database format best suited to the needs of the analytical mass spectrometry community. The spectrum of table 1 illustrates the database format proposed here. The precepts of the protocol are also applicable to other types of tandem mass spectrometers which have strong focusing properties (e.g., quadrupole-hexapole-quadrupole MS/MS), so long as the energy range used for the pertinent ion chemistry is the same as for XQQ instruments.

The kinetics notation and nomenclature developed in reference [9] are used throughout this paper.

2. General Background

As has been demonstrated [11]–[16], dynamically-correct branching ratios can be measured in XQQ instruments when the key MS/MS instrument parameters [9] are properly selected to account for reaction-induced mass discrimination [9] within Q2 and the intrinsic mass discrimination within the Q3 mass analyzer.

Table 1. Proposed CBRIS[1] database format[2,3]

Parent Ion: $C_2H_3O^+$ (m/z 43)[4,5] Notes: 9, 99, 999[6]
Source Compound: 2,3-butanedione (99.9%)
Ionization Mode: 70 eV electrons

E_{CM} (eV)	σ (Å^2)	α (13^+)	β (14^+)	γ (15^+)	δ (26^+)	ϵ (27^+)	ζ (28^+)	η (29^+)
2.4	15 [20]	0	0	0.999 [2]	0	0	0	0.0010 [50]
19.3	22 [10]	0.0127 [15]	0.0493 [6]	0.915 [2]	0.0101 [7]	0.0013 [10]	0.0005 [35]	0.0114 [7]
38.6	21 [10]	0.0227 [10]	0.0750 [6]	0.839 [2]	0.0436 [6]	0.0055 [20]	0.0055 [20]	0.0086 [15]

[1] CBRIS=Characteristic Branching Ratios of Ionic Substructures.
[2] For this example we show the branching ratios ($\alpha-\eta$) vs the center-of-mass collision energy (E_{CM}) for the CAD of ($C_2H_3O^+$) from the source compound biacetyl [16].
[3] The numbers in the square brackets represent the maximum uncertainty in the cross section σ and in the branching ratios ($\alpha-\eta$), expressed as a percentage of each σ and of each branching ratio {e.g., for biacetyl at E_{CM}=2.4 eV, the maximum uncertainty in γ is $\pm([2\%]/100)\gamma$; i.e., $\gamma=0.999\pm0.02$}.
[4] A reference citation would be provided for each CAD spectrum to identify the source of the data.
[5] For the CAD of any given parent ion (e.g., $C_2H_3O^+$), appropriate corrections must be made for contributions from the concurrent CAD of isobaric ions (e.g., $C_3H_7^+$), regardless of their source. The isobaric ions may be co-produced in the ion source (i) from the source compound (e.g., ionization of $CH_3C(O)C_3H_7$ will produce both CH_3CO^+ and $C_3H_7^+$) and/or (ii) from a neutral impurity in a source compound (e.g., for a butanol impurity in a 2-butanone source compound, the butanol generates $C_3H_7^+$, while the 2-butanone generates CH_3CO^+). Fortunately, the CAD spectra of CH_3CO^+ and $C_3H_7^+$ are easily distinguishable [16]. That is, for the CAD of $C_3H_7^+$, $C_2H_3^+$ (m/z 27) is the major CAD fragment for $E_{CM}\cong2-80$ eV. By contrast, for the CAD of $C_2H_3O^+$, $C_2H_3^+$ is not produced at E_{CM}=2.4 eV, and is only a very minor fragment for $E_{CM}>2.4$ eV. Unfortunately, even minor impurities can contribute disproportionately to the CAD spectrum of a source compound because of differences in the CAD dynamics of isomeric and/or isobaric ions. Because of this problem, it is advisable that both the source compound and the target gas be of high purity (>99.95%). Otherwise, the impurities must be characterized so that appropriate corrections can be made for their contribution to the observed CAD spectrum.
[6] The *Notes* field would be used to refer a user of the database to any information of special significance about the parent ion (e.g., structure of the ion, etc.). The notes enumerated in all the *Notes* fields of the CBRIS database would be collected together in a separate "Notes Appendix". For the example given here, Notes 9, 99, and 999 would be found in the Notes Appendix, and might contain the following types of information.

Note 9: For a given E_{CM}, the branching ratio for each fragment ion is substantially the same for all CH_3CO-X source compounds (e.g., biacetyl, acetone, acetophenone, etc.) [16]. The reactant ion entering Q2 appears to be pure CH_3CO^+ in every case [16].

Note 99: The energy dependence (magnitude and direction) of the branching ratios is distinctly different for the isobars $C_2H_3O^+$ and $C_3H_7^+$ [16]. Hence, one can readily distinguish $C_2H_3O^+$ from $C_3H_7^+$.

Note 999: One can readily distinguish ethanol, oxirane, and cis-2,3-epoxybutane from each other, and from CH_3CO-X source compounds on the basis of the energy dependence of the branching ratios for the CAD of $C_2H_3O^+$ [16].

The systems studied in this laboratory include charge transfer and dissociative charge transfer reactions, and CAD.

Charge Transfer:

$$Ne^+ + Ne \rightarrow Ne + Ne^+ \quad [11],$$

$$Ar^+ + Ar \rightarrow Ar + Ar^+ \quad [12],$$

and $$Ar^+ + N_2 \rightarrow Ar + N_2^+ \quad [13]$$

Dissociative Charge Transfer:

$$N_2^+ + SF_6 \rightarrow N_2 + SF_x^+ + (6-x)\,F$$

(where $x=1-5$) [14]

CAD:

$$(CH_3)_2CO^+ \xrightarrow{\text{Ar CAD}} CH_3CO^+ + CH_3 \quad [15]$$

$$CH_3CO^+ \xrightarrow{\text{Ar CAD}} CH_3^+ + CO \quad [16]$$

Note that for collision energies $E_{LAB} \simeq 1-200$ eV in the Laboratory (LAB) frame of reference, charge transfer reactions are experimentally equivalent to a "worst-case" CAD reaction system because they take place at large impact parameters with near-zero momentum transfer. That is, the product ions of a charge transfer reaction are formed essentially at rest (thermal energies) within Q2 [17]–[20].

The studies in our laboratory led to the development of a kinetics-based measurement protocol for the generation of standard XQQ spectra. Using the protocol, one can obtain, for the first time, accuracy and precision for CAD measurements within XQQ tandem mass spectrometers. A round robin exercise, the NIST-EPA International Round Robin [21], was organized to ascertain which commercially-available XQQ instruments are capable of generating dynamically-correct (i.e., instrument-independent) spectra. Appendix 1 contains the actual round-robin protocol which was disseminated to 22 laboratories worldwide (including the six XQQ instrument manufacturers). Analysis of the round robin data from six participants indicates that at least 50% of the QQQ instruments which have been sold and are currently in the field can provide such standard spectra [21].

Instruments which can generate dynamically-correct results with the round robin protocol of Appendix 1 can be used to develop a generic, standardized CAD spectral database (or library) based on Characteristic Branching Ratios of Ionic Substructures (CBRIS) (analogous to the use of group frequencies in infrared spectroscopy; see section 5.1). Hence, members of the analytical mass spectrometry community who have such instruments could use the kinetics-based measurement protocol detailed in this paper to generate and contribute instrument-independent CAD spectra of species studied during the course of their work. Contributed CAD spectra (to be sent to this author) would be included in the NIST-EPA Standardized CAD Database currently being developed in our laboratory. The latter would be disseminated by NIST to the analytical mass spectrometry community. To facilitate the critical evaluation of contributed spectra, a dynamically-correct CAD spectrum of a well-studied "model" compound (e.g., n-butylbenzene) should also be submitted.

3. Technical Basis for Protocol

Here we summarize the technical basis for the kinetics-based measurement protocol. For a more detailed treatment, the reader is referred to references [2]–[9].

3.1 Kinetics

With reference to the following general reaction sequence:

$$A^+ + B \rightarrow C^+ + S \qquad (\propto \sigma)$$

$$\rightarrow D^+ + T \qquad (\beta\sigma)$$

etc.

equations (1)–(3) are applicable under pseudo-first order $\{[B]_0 >> [A^+]_0\}$, *single-collision* conditions for a reaction zone of length L wherein the number density of the target gas is [B] and the "target thickness" is $[B]L$. Here $\sigma\ (= \propto\sigma + \beta\sigma + ...)$ is the total cross section for the $A^+ + B$ interaction, and the sum of the branching ratios $\propto + \beta + ...$ is equal to 1.

Reactant Ion Decay:

$$\ln Y \equiv \ln \{[A^+]_0/[A^+]\} = \sigma[B]L \qquad (1)$$

and

Product Ion Formation:

$$\ln W_\propto \equiv \ln \{\propto [A^+]_0/(\propto [A^+]_0 - [C^+])\} = \sigma[B]L \qquad (2)$$

$$\ln W_\beta \equiv \ln \{\beta[A^+]_0/(\beta[A^+]_0 - [D^+])\} = \sigma[B]L \qquad (3)$$

etc.

In the case of CAD, A^+ corresponds to the parent ion; B corresponds to the target gas; C^+, D^+, etc. are the progeny fragment ions; and S, T, etc. are the neutral fragments complementary to C^+, D^+, etc.

Under dynamically-correct conditions, the rate of reactant ion decay equals the rate of product ion formation. That is $\ln Y = \ln W_\propto = \ln W_\beta$, etc. Then the product ion intensities C^+, D^+, etc. are related to the extent of consumption of the reactant ion $\{[A^+]_0 - [A^+]\}$ by eqs (4), (5), etc.

$$[C^+] = \propto \{[A^+]_0 - [A^+]\} \qquad (4)$$

$$[D^+]=\beta\{[A^+]_0-[A^+]\} \quad (5)$$

etc.

3.1.1 Dynamically-Correct Representation If the key MS/MS parameters [9] of an XQQ instrument can be tuned so that data generated by the instrument conform to equations (1)-(5) [viz., so that $\propto+\beta+\gamma+\ldots=1.00$], then the instrument can provide a dynamically-correct representation of any reaction studied within it. That is, by using eqs (4'), (5'), etc., the instrument would provide a measure of the branching ratios equivalent to those that, in principle, would be observed at the scattering center of a molecular beam machine.

$$\propto=[C^+]/\{[A^+]_0-[A^+]\} \quad (4')$$

$$\beta=[D^+]/\{[A^+]_0-[A^+]\} \quad (5')$$

etc.

3.1.2 Kinetics Constraints The selection of key MS/MS parameter settings is constrained by the kinetics prerequisite for $\propto+\beta+\gamma+\ldots=1$ (see reference [9]). This prerequisite necessitates that:

(a) each product ion be formed only by the primary reaction (no secondary sources; pseudo-first order, single-collision conditions)
(b) all ions be detected with equal sensitivity (requires Conversion Gain corrections for each detector; see sec. 4)
(c) there be no scattering losses because of unreactive collisions (must have high ion containment within Q2; approximately 100% collection efficiency for product ions and unreacted projectiles)
(d) corrections be made for differences in ion containment (transmission) within the Q2Q3 structure.

3.2 Instrumental Parameters

To accomplish $\propto+\beta+\gamma+\ldots=1.00$, the key MS/MS parameters must be properly selected to obviate discrimination against product ions because of:

(a) Reaction-Induced Mass Discrimination (RIMD) within Q2 (refer to sec. 3.2.1),
(b) Intrinsic Mass Discrimination (IMD) within Q3 (refer to sec. 3.2.2), or
(c) the kinetic energy of product ions entering Q3 (refer to sec. 3.2.3).

We shall use the terms "RIMD-free" and "IMD-free" to refer to branching ratios $\propto$, β, etc. which have been measured in concordance with the precepts detailed next for (a)–(c). That is, to be RIMD-free and IMD-free, the instrument parameters discussed below in sections 3.2.1–3.2.3 have to be tuned and returned iteratively until $\propto+\beta+\gamma+\ldots\simeq1.0\pm0.1$.

3.2.1 Reaction-Induced Mass Discrimination (RIMD) Within Q2 The rf amplitudes of Q1, Q2, and Q3 are characterized here by the Mathieu parameters q_1, q_2, and q_3, respectively (for further information, see references [2]–[5]). In this discussion q^{max}_{react} and q^{max}_{prod} are used to represent, respectively, the values of q_2 which correspond to the maximum ion transmission through Q2Q3 for the reactant (projectile) ion of mass m_{react} and for each product ion of mass m_{prod}. The subscripts "react" and "prod" designate, respectively, the reactant ion A^+ and the product ion C^+ (or D^+, etc.).

Within Q2, $m_{prod}/m_{react}=q_{react}/q_{prod}$ [9]. Therefore, low-mass daughters are not detected when $m_{prod}/m_{react}<q_{react}/0.908$ since ion trajectories are unstable when $q_2>0.908$ [5]. This means that the signal for each product ion must be measured at its respective q^{max}_{prod}. For each product ion, its corresponding $\{[A^+]_0-[A^+]\}$ must also be measured at that same q^{max}_{prod}. That is, with reference to eq (4'), $\propto$ must be determined by measuring $[C^+]$ and $\{[A^+]_0-[A^+]\}$ at the q^{max}_{prod} for C^+; with reference to eq (5'), β must be determined by measuring $[D^+]$ and $\{[A^+]_0-[A^+]\}$ at the q^{max}_{prod} for D^+; etc. This must be done to compensate for the differences in ion containment efficiencies within the Q2Q3 structure.

For example, consider the CAD of a parent ion of m/z 196 which fragments to progeny ions of m/z 15, m/z 42, and m/z 86 [5]. In this case $\propto$ must be determined by measuring $[15^+]$ and $\{[196^+]_0-[196^+]\}$ at the q^{max}_{prod} for 15^+; β must be determined by measuring $[42^+]$ and $\{[196^+]_0-[196^+]\}$ at the q^{max}_{prod} for 42^+; etc. The reader may wish to consult reference [5] for a more detailed exposition.

In principle, if XQQ instruments were well behaved, all measurements could be made at the q^{max}_{prod} for the progeny ion of lowest mass (m/z 15 for the example above [5]). However, because of ion-optical imaging (focusing) problems within the Q2Q3 structure, one usually observes oscillations in the ion intensity as q_2 is varied [5]. Consequently, measurements of $[C^+]$, $[D^+]$, etc. and their respective $\{[A^+]_0-[A^+]\}$ must be made at the local maxima closest to the q^{max}_{prod} of each product ion.

3.2.2 Intrinsic Mass Discrimination (IMD) within Q3 The resolution controls for Q3 must be varied as necessary to compensate for the mass discrimination intrinsic to Q3 {cf. [2]: p. 100, p. 105 (fig. 5.9), and p. 143–144}.

3.2.3 The Kinetic Energy of Product Ions Entering Q3 It is now recognized that in the LAB frame of reference the translational energy of product ions E_{prod} is generally related to the collision energy of the projectile (reactant) ion E_{react} by:

$$E_{prod} \simeq (m_{prod}/m_{react})^n E_{react}, \quad (6)$$

where $n \simeq 1-2$ for CAD processes studied to date [8]. Hence, if $m_{prod}/m_{react} << 1$, low-mass daughters exiting Q2 will have low kinetic energies. Consequently, the Q3 rod offset (pole bias) must be set sufficiently low with respect to the Q2 rod offset so that no low-mass, low-energy product ions are denied entry to Q3 by the Q3 potential barrier. On the other hand, the Q3 potential barrier must be sufficiently high to provide adequate resolution within Q3 [8]. The reader may wish to consult references [7] and [8] for a more detailed exposition with reference to the selection of the appropriate Q3 rod offset.

4. Kinetics-Based Protocol for MS/MS Measurements

In this section we detail the generic protocol used to measure instrument-independent CAD spectra in XQQ instruments. The reader is referred to the caveats detailed in items 1–9 of the *Precautions* in Appendix 1.

(a) The protocol of Appendix 1 (for the NIST-EPA International Round Robin) must first be used to validate that any particular XQQ instrument can provide a dynamically-correct (i.e., instrument-independent) representation of ion-molecule reactions. If the instrument cannot pass the protocol (i.e., it cannot provide a dynamically-correct representation), one should not proceed any further until one has eliminated the ion-optical defect(s) so that the instrument can pass the protocol. If the instrument can provide a dynamically-correct representation, then the measurements for Part 1 of the round-robin protocol of Appendix 1 will provide an in situ calibration of the target thickness of the XQQ instrument.

(b) For all MS/MS measurements, one must use a gas target thickness within the single-collision regime [<2 cm-mtorr (<0.267 cm-Pa) for Ar]. For CAD, use an Ar gas target since it has been demonstrated [22] that the equivalent excitation energy (i.e., the equivalent internal energy imparted to a parent ion) is significantly less for a polyatomic target than it is for a monatomic target. However, one may also use other inert gas targets (He, Ne, Kr, or Xe) as necessitated by the collisional energy requirements since it has been demonstrated that the equivalent excitation energy is the same for the inert gases at any given center-of-mass energy E_{CM} [22]-[24] $\{E_{CM} = E_{LAB}\ [m_2/(m_1+m_2)]$, where m_1 and m_2 are, respectively, the masses of the reactant ion and of the gas target}.

(c) One must use a *fixed* operating voltage for the ion detector (multiplier, Daly detector, etc.). The fixed voltage should provide the best compromise between the signal-to-noise ratio (S/N) of A^+ and the S/N of C^+, D^+, E^+, etc.

(d) One must make Conversion Gain measurements if an instrument uses analog current measurements. Conversion Gain is the ratio of the electron current output from an electron multiplier relative to the ion current input. The Conversion Gain measurements are used to correct for differences in mass-dependent detector response. If the instrument uses *true* ion pulse counting, Conversion Gain measurements are *not* needed [i.e., ignore instruction (d) and continue with instruction (e)].

Warning: Some instruments use analog current measurements, but report the ion intensities as equivalent ion count rates within their data systems. Such instruments still require Conversion Gain measurements.

Note: If possible, one should adjust the Conversion Gain of the ion detector so that one attains a mass-independent detector response. That is, so that the Conversion Gain is the same for a projectile ion and for its lowest-mass product ion (e.g., for CAD) or highest-mass product ion (e.g., for neutral gain reactions). This might be accomplished, for example, by adjusting the operating voltage of a high-voltage (e.g., 20–30 kV) conversion dynode which is used in conjunction with an electron multiplier. If it is not possible to attain a mass-independent detector response, then one must make corrections for difference in Conversion Gain for each parent ion and for each product ion.

To measure Conversion Gains, one may use a procedure analogous to that used for instructions 30–39 in Part 2 of the NIST-EPA round robin protocol in Appendix 1. However, to ensure that the most reliable correction factors are obtained, the mass-dependent Conversion Gain measurements would have to be made under actual operating conditions (viz., with the conversion dynode and electron multiplier at high voltages). This might be done by measuring the ion current striking the conversion dynode and relating it to the output current from the electron multiplier. One would have to demonstrate, however, that there is a one-to-one correspondence between the ion current input and the electron current output, independent of ion structure.

Note: For the rest of the instructions which follow, it is presumed that the ion signals correspond to a mass-independent detector response. That is, if necessary, the ion signals have been corrected for differences in Conversion Gain efficiency.

(e) Adjust the appropriate ion-optical elements (e.g., the Q1 rod offset for QQQ instruments) so that (i) $[B]_0 >> [A^+]_0$ and (ii) the energy spread of the projectile ions entering Q2 is minimized ($\leqslant$3 eV for 50% of the ions). (Refer to item 3 of the *Precautions* from the NIST-EPA round robin protocol in Appendix 1.) Measure the Q2 stopping curve in a manner analogous to that prescribed in instructions 8–10 of Part 1 of the NIST-EPA round-robin protocol in Appendix 1.

(f) From the optimum Q2 stopping curve measurements determine E_{50} (corresponds to the Q2 rod offset that stops 50% of the reactant ions). Then set the Q2 rod offset equal to $E_{50}-E_{LAB}$, where E_{LAB} is the requisite collision energy (in LAB coordinates).

(g) One must use only a "daughter-scan" mode. That is, Q1 is tuned to the peak position which corresponds to the maximum ion intensity at the m/z of the projectile ion while Q3 scans over the peak which corresponds to the m/z of a product ion. The q_2 must be referenced to q_1 (i.e., to q_{react}) rather than to q_3 (i.e., to q_{prod}). Use a scan window of ca. 4–10 amu so one can see the entire mass peak (baseline-to-baseline).

Note: To ensure consistent measurements for the duration of each experiment, make sure Q1 is staying tuned to the peak position for the projectile ion intensity; this can be done by varying the Q1 mass command to maximize the ion signal being viewed within the Q3 scan window. Use the same *fixed* operating voltage for the ion detector as was used for instruction 4 (c).

(h) One then adjusts iteratively the resolution parameters for Q3, and the Q3 rod offset as necessary to approximate $\propto+\beta+\gamma+...\simeq 1.0$ for the $\propto$, β, ..., etc. measured in concordance with the precepts detailed in sections 3.2.1–3.2.3. To optimize the precision of all measurements, ion signals should be measured in "back-to-back" units [cf. item 6 (iii) of the *Precautions* from the NIST-EPA round-robin protocol in Appendix 1]. For example, for a fixed [B]L measure:
$[C^+]$, $[A^+]$, and $[A^+]_0$ at the q_{prod}^{max} for C^+;
$[D^+]$, $[A^+]$, and $[A^+]_0$ at the q_{prod}^{max} for D^+; etc.

Note: One must make appropriate corrections for any background contributions to $[C^+]$, $[D^+]$, etc. which may be observed in the absence of added target gas. Such background contributions can arise from decompositions of A^+ (to produce C^+, D^+, etc. via CAD or RIF [9]) occurring between the rear of Q1 and the front of Q3. Such background CAD or RIF may be induced by the interaction of A^+ with plumes of gas emanating from the ion source.

(i) In practice, instructions (b)–(h) provide IMD-free and RIMD-free estimates for the branching ratios of fragment ions, except for very minor fragment ions adjacent to major ions. The resolution is not adequate for obtaining dynamically-correct estimates for the branching ratios of very minor fragment ions adjacent to major ions. Consequently, the resolution must be increased for each group of ions which contains a minor ion adjaent to a major ion, and complementary measurements must be made for the branching ratios of minor fragment ions within each group. Each group contains only fragment ions which are in close proximity (e.g., m/z 13–15), so that the measurements for each ion in the group are still IMD-free and RIMD-free within that group. To relate these individual group measurements to the overall CAD spectrum [viz., to the entire range of masses from the m/z of the reactant (parent) ion down to the m/z of the lowest-mass product ion], the measurements for each group must be referenced to the IMD-free and RIMD-free estimate for the branching ratio of a major fragment ion within that group. For example, for $E_{CM}\simeq 2-40$ eV, the CAD of $C_2H_3O^+$ (m/z 43) from biacetyl pro-

duces fragment ions at the following m/z: 13, 14, 15, 26, 27, 28, 29. The fragment ions at m/z 13 and 14 are minor compared to the major fragment ion at m/z 15 (refer to table 1). Therefore, m/z 13–15 are measured under well-resolved conditions and referenced to the IMD-free and RIMD-free estimate for the branching ratio of the fragment ion at m/z 15. Similarly, the fragment ions at m/z 27 and 28 are referenced to the fragment ions at m/z 26 and/or 29.

(j) Repeat (b)–(i) as necessary to accomplish $\propto+\beta+\gamma+...\simeq 1.0\pm 0.1$ for each E_{CM}, as necessitated by the reaction dynamics.

5. Proposed Format for MS/MS Database

Table 1 shows a typical CAD spectrum (measured with the protocol of sec. 4 [16]) in the format proposed for presentation of CBRIS.

5.1 Advantages

The advantages of this CBRIS database format are:

(a) The partial cross sections $\propto\sigma$, $\beta\sigma$, etc. can characterize both known and unknown species (so long as the unknown species contain ionic substructures for which the CAD cross sections and product identities are known). Therefore, it may be possible to assign the structure of an *unknown* species on the basis of the absolute cross sections σ_{ij}, σ_{jk}, etc. for the CAD of *known* ionic substructures i, j, k, etc. That is, this proposed use of CBRIS in MS/MS is analogous to the use of group frequencies in infrared spectroscopy.

(b) Characterization of an unknown compound by using CBRIS does not require that the compound be in the CBRIS database. By contrast, to characterize an unknown by spectral matching within a "library", the compound must usually be in the library. In this regard, development of a *database* of CBRIS for all substructures (or a subset thereof) would be very much more tractable than the development of a *library* of CAD spectra for all the source compounds that contain all the substructures (or a subset thereof). For example, consider the simplistic analogy where compounds correspond to words, and substructures correspond to letters: more than 500,000 words can be composed with only 26 letters of the alphabet.

(c) The format is compatible with its use in expert systems. This should facilitate rapid real-time analysis of unknowns within computer-controlled field instruments.

(d) End users are involved directly in its evolution by using critically evaluated cross sections already in the database and by submitting new cross sections for inclusion in the database.

6. Conclusions

A kinetics-based measurement protocol can provide accuracy and precision for CAD measurements within XQQ tandem mass spectrometers. This protocol can be used to develop a dynamically-correct (i.e., instrument-independent) MS/MS database (or library) for XQQ instruments.

7. Acknowledgments

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Appendix 1. NIST-EPA Round Robin for XQQ Instruments (QQQ, BEQQ, etc.): A Test Protocol to Assess Which Instrument Designs Provide Instrument-Independent (Dynamically-Correct) Performance

Note: This appendix is the full text of the actual document which was sent to, and was used by, the participants in the NIST-EPA International Round Robin. The round-robin results have been published elsewhere [21]. *This document may be photocopied. Prospective participants may submit test data to the author anytime for this ongoing evaluation project.*

This round robin is being coordinated by Dr. Richard I. Martinez of the U.S. National Institute of Standards and Technology (NIST). It is sponsored by the Environmental Monitoring Systems Laboratory (EMSL) of the U.S. Environmental Protection Agency (EPA).

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Objective

To assess which XQQ instrument designs can be used to generate a generic, instrument-independent MS/MS database. To do so, an XQQ instrument (QQQ, BEQQ, etc.) must provide a dynamically-correct (instrument-independent) representation of any ion-neutral interaction (e.g., CAD, etc.) studied within its Q2Q3 structure. The prerequisites for obtaining dynamically-correct branching ratios within XQQ instruments have been detailed in reference [9].

Data Analysis

To ensure consistency, all data will be analyzed by the round-robin coordinator. The participants will provide only "raw data" on the forms provided with the test protocol. To perform the analysis, the raw data will have to include information about such technical specifications as field radius, rf frequency, etc. Please submit one completed copy of the *Questionnaire* for each XQQ instrument included in the round robin.

Confidentiality

All information provided by participants will be confidential. No proprietary information will be divulged. No participant or instrument manufacturer will be identified (the data files will be encrypted with code letters, numbers, and symbols known only to the round-robin coordinator). All test results will be discussed only in generic terms.

Summary of Test Protocol

The test protocol is based on (i) the concepts detailed in reference [9], and (ii) the use of the ion-neutral reaction kinetics of references [12] and [14].

The following is a synopsis of the two major components of the test protocol. The nomenclature used herein is defined in references [9], [12], and [14].

Part 1

Purpose

(i) To determine if the reaction kinetics are well controlled (i.e., no back reactions, no scattering losses, minimal fringing fields, no mass discrimination, well-defined gas target, etc.) within each XQQ instrument. The symmetric charge transfer reaction $^{36}Ar^+ + {}^{40}Ar \rightarrow {}^{36}Ar + {}^{40}Ar^+$ is used (see reference [12]). In this case there is no reaction-induced mass discrimination (defined in reference [9]).

(ii) To calibrate the response of the pressure sensor closest to the participant's collision region in terms of the effective target thickness $[Ar]L_{eff}$ within the collision region (L_{eff} is the effective pathlength of the complex oscillatory trajectory traversed by a projectile ion through the CAD target gas within Q2). This is done to ensure all participants use the same effective target thickness measurements.

Glossary

Here we describe some terms used below.

NISTCALPLOT A calibration curve of ln Y (=ln W) vs effective target thickness $[Ar]L_{eff}$. NISTCALPLOT (fig. 1) is included below for use with the test protocol.

P/XQQ The nominal pressure indicated by some sensor located closest to the participant's collision region (see *Precaution* 8).

ARLEFF/LNY The target thickness $[Ar]L_{eff}$ which is derived from NISTCALPLOT for a corresponding ln Y value measured by a participant for a given P/XQQ.

ARLEFF/LNW The target thickness $[Ar]L_{eff}$ which is derived from NISTCALPLOT for a corresponding ln W value measured by a participant for a given P/XQQ.

XQQCALPLOT A graph containing a plot of ARLEFF/LNY vs P/XQQ and a plot of ARLEFF/LNW vs P/XQQ.

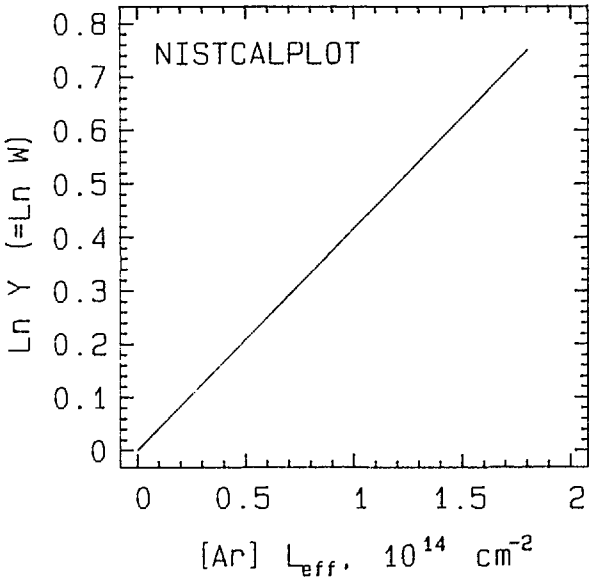


Figure 1. Calibration curve of ln Y (=ln W) vs effective target thickness $[Ar]L_{eff}$.

Method

Using several different pressures (P/XQQ) of Ar target gas, each participant measures ln Y *and* ln W for the reaction $^{36}Ar^+ + {}^{40}Ar \rightarrow {}^{36}Ar + {}^{40}Ar^+$. NISTCALPLOT is then used to convert the participant's ln Y and ln W measurements to the corresponding target thicknesses ARLEFF/LNY and ARLEFF/LNW, respectively. These data are then used to prepare the calibration graph XQQCALPLOT. If the kinetics are well controlled within the participant's XQQ instrument, then the two plots of ARLEFF/LNY vs P/XQQ and ARLEFF/LNW vs P/XQQ should be superimposable.

Part 2

Purpose

To assess how well one can correct for reaction-induced mass discrimination and for strong ion-optical imaging (focusing) problems within the Q2Q3 structure (i.e., how well one can control the key MS/MS parameters in different XQQ instrument designs) (see reference [9] for further information).

Method

Each participant measures ln *Y and* ln *W* for the reaction $N_2^+ + SF_6 \rightarrow N_2 + SF_5^+$ as a function of the pressure P/XQQ of the SF_6 gas target (cf. reference [14]).

Data Format

Different types of data are requested within the test protocol. Most of the test data to be provided by the participants will consist of "filling-in-the-blanks" in the spaces provided with the test protocol.

For laboratories with more than one XQQ instrument participating in the round-robin test, please submit a separate set of data for each XQQ instrument (use photocopies of this test protocol document to record each separate set of data).

Precautions

1. Manual vs Automated Control

Some very sophisticated XQQ systems have automated ("intelligent") self-tuning capabilities (e.g., mass calibration, etc.), automated instrument control (e.g., "programmed ion optics", MS/MS mass scan modes, etc.) and automated data acquisition, etc.

To provide the best possible assessment of instrument *Hardware* design (without obfuscation by software artifacts), and to ensure consistency among the data submitted, participants must *not* use any of the automated capabilities.

Instrument control and data acquisition should be as close to "manual" control as is possible with your instrument. You may use a "hybrid" control system wherein you are "manually" controlling the parameters [e.g., programmable "soft-knobs" (EXTREL[1]) or "tuning tables" (Finnigan TSQ70) are used to vary the dc voltage which is being applied to a lens via a digital-to-analog converter (DAC)]. However, use only a single "tuning table" with "flat" (constant) parameter settings; don't use "programmed ion optics". Please mark the top of the first page of the submitted data with the following label: *Manual Instrument Control and Data Acquisition.*

However, for any one XQQ instrument being tested, participants are welcome to submit a *second* set of data to assess possible artifacts in the instrument control and data acquisition software. Please mark the top of the first page of the submitted data with the following label: *Automated Instrument Control and Data Acquisition.*

If your system has only automated capabilities (i.e., there is absolutely no way that it can be made to function in a manual or hybrid mode of operation for instrument control and data acquisition), please mark the top of the first page of the submitted data with the following label: *Non-Manual Instrument Control and Data Acquisition.*

[1] Certain commercial equipment, instruments, and materials are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the material, instruments, or equipment identified is necessarily the best available for the purpose.

2. Actual Voltage Measurements

The actual voltages of all essential ion-optical elements [rod offset (pole bias) of Q1, Q2, Q3; lens potentials; etc.] must be measured with a voltmeter at the appropriate measurement test points closest to each ion-optical element. Consult the manufacturer for the location of each test point and the method of measurement that you should use to ensure correct values (e.g., to measure actual rod offsets, you may have to disconnect the inputs for mass command and/or resolution control and/or ΔM control). Please make actual voltage measurements to validate any voltage information provided by a computer system via an analog-to-digital converter (ADC).

3. Q1 Rod Offset and Projectile Energy Distribution

To be kinetically meaningful, participants must ensure:

(a) that $[B]_0 >> 100[A^+]_0$ (in molecules cm^{-3} within Q2; ion intensity data are converted to the approximate ion concentrations with reference to the defining aperture which provides entry into Q2),
(b) that the measured reactivity can be attributed to a well-characterized state of the projectile ion A^+, and
(c) that the translational energy distribution of the projectile ion entering Q2 is reasonably narrow (cf. Q2 stopping curve data in references [12] and [14]). [Unfortunately, narrowing the energy distribution of the projectile ion can produce ion-optical imaging (focusing) problems within Q2 if the XQQ instrument has restrictive interquadrupole apertures (see reference [9]).]

For QQQ instruments, tasks (a)–(c) can be accomplished by over-resolving Q1 (i.e., increasing the resolution of Q1 to produce a sharp, narrow peak) and by raising the Q1 rod offset close to the ion source potential. The effect of these actions is to: (i) discard a large fraction (>90%) of A^+, (ii) delay the transit of A^+ through Q1 (this provides sufficient time for excited electronic states of the N_2^+ used for *Part 2* to be quenched by radiative transitions prior to their entry into Q2), and (iii) reduce the energy spread of the ions exiting Q1 by cutting out low-energy ions. Unfortunately, rf-pickup within each quadrupole mass filter tends to broaden the energy distribution of the projectile ion as it traverses Q1, Q2, and Q3. Therefore, a high-energy tail is usually observed.

4. Q3 Rod Offset

To achieve $\ln W = \ln Y$, one must have very high ion-collection-efficiency ($\simeq$100%). Consequently, the Q3 rod offset must be biased very *negatively* with respect to the Q2 rod offset to draw ions out of Q2. This will result in very broad, poorly resolved mass peaks (reference [8] shows examples of how the Q3 rod offset affects peak shapes). Throughout each *Part* of the test protocol, you must keep the Q3 rod offset biased as negatively as necessary so that $[C^+] \simeq [A^+]_0 - [A^+]$.

5. Tuning q_2

The rf amplitude of Q1, Q2, and Q3 is characterized here by the Mathieu parameters q_1, q_2, and q_3, respectively (for further information, see references [2]–[5]). Some instruments have a separate rf/dc generator (quadrupole controller/power supply) for each of the three quadrupole rod assemblies (Q1, Q2, and Q3); some do not. Some can reference q_2 to q_3 *and/or* to q_1 (i.e., one can vary q_2/q_1 or q_2/q_3 from 0–1; in some instruments the ratio is fixed at $q_2/q_1 = 0.5$ or $q_2/q_3 = 0.5$). Some instruments reference q_2 to the ion transmission cut-off which occurs at $q_2 \simeq 0.908$ [this latter mode of tuning is somewhat risky; the rf-pickup within Q2 can make it difficult to distinguish the true cut-off at $q_2 \simeq 0.908$ from the small, but significant contribution of ions in the high energy tail which are transmitted through Q2Q3 even though the nominal (apparent) value is $q_2 > 0.908$].

In general, tune q_2 by following the recommendations of the manufacturer of your XQQ instrument (please complete the questionnaire regarding modes of operation for your XQQ instrument). However, to ensure experimental consistency among participants, please validate your q_2 values relative to q_1 and/or q_3 (i.e., remember that whenever Q1 or Q3 are operated in a well-resolved mode and are tuned to any m/z, then the mass peak position corresponds to $q_1 \simeq 0.706$ or $q_3 \simeq 0.706$ for that m/z).

One can accomplish the validation of q_2 values with a simple potentiometer divider circuit if the instrument can be operated in a manual or hybrid mode. For example, in some instruments a *Mass Command* input dc voltage (typically 0–10 V) is used to control the rf amplitude of a quadrupole mass filter. This 0–10 V is usually supplied by a DAC which may be controlled by a computer via a programmable soft-knob. Here we use MC1, MC2, and MC3 to designate, respectively, the 0–10 V *Mass Command* input voltages for Q1, Q2, and Q3. Then the divider potentiometer can be used to vary q_2/q_1 ($\simeq$MC2/MC1) or q_2/q_3 ($\simeq$MC2/MC3). Consult your manufacturer for the location of the inputs analogous to MC1, MC2, and MC3.

If the manufacturer asserts there is absolutely no possible way to vary q_2 within your instrument (i.e., one cannot vary q_2/q_1 or q_2/q_3), please indicate how q_2 is controlled by the manufacturer (i.e., does the manufacturer use a fixed value of q_2/q_1 or $q_2/q_3 \simeq 0.5$, or ?). Also, please mark the top of the first page of the submitted data with the following label: q_2 *Not Varied.*

6. Acquisition of Ion Intensity Data

(i) Mode of Operation

Use only a "daughter-scan" mode [i.e., q_2 referenced to q_3; Q1 tuned to the peak position which corresponds to the maximum ion intensity at the m/z of the projectile ion; Q3 scanning over the peak which corresponds to the m/z of the product ion (use a scan window of ca. 4–10 amu) so you can see the entire mass peak (baseline-to-baseline)].

Note: To ensure consistent measurements for the duration of each experiment, make sure Q1 is staying tuned to the peak position for the projectile ion intensity; this can be done by varying the Q1 mass command to maximize the ion signal being viewed within the Q3 scan window.

(ii) Signal and Background Measurements

For the reasons discussed in 1 above, all ion signal intensities must be acquired *manually*. To do so, you must use a display which shows the *complete* mass spectral peak shape for a single mass peak (i.e., baseline-to-baseline display of ion intensity vs m/z for a single mass peak). For this, you can use either an external oscilloscope connected to the output of your detector chain, or whatever mass spectral display your system provides on its CRT.

For each mass peak, use arbitrary units (e.g., CRT divisions) to measure the ion intensity at the peak. However, report the ion intensities in relative units by making appropriate corrections for differences in amplifier gain, scope attenuation, etc. [e.g., an ion intensity of *1.00 relative units* could correspond to (a) 1 CRT division with an amplifier gain of $\times 1$ and a scope attenuation of $\times 1$, etc. or (b) 10 CRT divisions with an amplifier gain of $\times 100$ and a scope attenuation of $\times 10$].

For the measurement of *background* alone, the ion intensity is measured at the mass peak position in the absence of the ion of interest. For the measurement of *signal + background*, the ion intensity is measured at the mass peak position in the presence of the ion of interest.

Note: Please follow the following guidelines to ensure the ion intensity measurements are kinetically meaningful, and to minimize long-term variations in gas flows, detector response, etc. Here source gas refers to the gas introduced into the ion source, and target gas refers to the gas introduced into Q2.

(a) Before making any ion intensity measurements in Part 1 or Part 2, allow sufficient "warm-up" time to ensure all instrumental components, ion source, gas flows, etc. have stabilized.

(b) Leave *everything* (source gas, ionizer filament, etc.) turned on at all times for the duration of all measurements in any one Part (the target gas is the only thing that should be turned on and off during the measurements).

(c) If possible, use a high-quality toggle valve or solenoid shut-off valve to turn the target gas on/off. (The shut-off valve should be located between the Q2 collision region and a high-precision needle valve). Thus, the target gas flow can be reset reproducibly to any given P/XQQ by presetting the needle valve. This will help to ensure high-accuracy "back-to-back" units for ln Y/ln W measurements.

(d) To make measurements of the *background* intensity at any m/z, block the Projectile Ion Beam (PIB). To do so, raise to a high positive voltage the potential of any ion-optical element (e.g., the rod offset of Q1 or Q2).

The following abbreviations are used throughout the protocol:
PIBOFF=Projectile Ion Beam OFF (projectile ion beam blocked; no ions reach the detector)
PIBON =Projectile Ion Beam ON (projectile ion beam unblocked; ions enter Q2)
TGOFF =Target Gas OFF (not flowing into Q2)
TGON =Target Gas ON (flowing into Q2)

(iii) ln Y and ln W Measurements

All ln Y and ln W data should be collected in *back-to-back units* to minimize long-term variations in gas flows, detector response, etc. For example, with reference to equations (1) and (2), one back-to-back unit would consist of items (a)-(g) below. Here q_{react}^{max} and q_{prod}^{max} represent, respectively, the values of q_2 which correspond to the maximum ion transmission through Q2Q3 for the reactant (projectile) ion A^+ and for the C^+ product ion. Note that q_{react}^{max} and q_{prod}^{max} must be known prior to making the ln Y and ln W measurements.
(a) tune q_2 to q_{react}^{max} for A^+.
(b) PIBOFF/TGOFF: measure background signal at $m/z(A^+)$.
(c) PIBON/TGOFF: measure $[A^+]_0$ at $m/z(A^+)$.
(d) PIBON/TGOFF: tune q_2 to q_{prod}^{max} for C^+; measure background signal at $m/z(C^+)$.
(e) PIBON/TGON: measure $[C^+]$ at $m/z(C^+)$; tune q_2 to q_{react}^{max}; measure $[A^+]$ at $m/z(A^+)$.
(f) repeat (c).
(g) repeat (b).

(iv) Detector Conversion Gain

Use a *fixed* operating voltage for your ion detector (multiplier, Daly detector, etc.). The fixed voltage used for measurements within *Part 1* can differ from the fixed voltage used for *Part 2*. But you must use the same fixed voltage for all back-to-back units within any one Part. For each Part, the fixed voltage should provide the best compromise between the S/N of A^+ and the S/N of C^+.

7. Target Gas Purity

The purity of the Ar and SF_6 target gases should be >99.99%.

8. P/XQQ Measurements

There are only two requirements for P/XQQ measurements: (1) that the sensor being used must provide a *reproducible, single-valued* response for any given target gas pressure of Ar, and (2) that you know the relative sensitivity of the sensor (i.e., its response factor) for SF_6 relative to Ar. For example, some instruments use a mass flowmeter to measure the flow rate of the target gas into the collision region. You could use the flowmeter response if you know its response factor for SF_6 and for Ar.

9. High-Vacuum Materials

No plastic tubing (teflon, etc.) should be used to introduce the high-purity target gas into the collision region within Q2. The target gas should flow only through materials normally used in high-vacuum applications (bellows valves, etc.). This will ensure that the ln Y and ln W measurements are not complicated by reactions of the projectile ion with impurities inadvertently admixed with the target gas. If you do have plastic parts in contact with the target gas, and can't substitute high-vacuum materials for the duration of this test, please mark the top of the first page of the submitted data with the following label: *Plastic Tubing Used*.

Test Protocol

Note: Before proceeding with the test protocol, please read the *Precautions* above, familiarize yourself with all the steps of the test protocol, and refer to references [9], [12], and [14] as necessary. To ensure consistency among participants, all tuning procedures and measurements must be carried out in accord with the *Precautions*. Please be sure to observe *Precaution 4*. If you have any questions, please call the round-robin coordinator.

Note: Record all ion intensities in *relative units (Precaution 6.)* in the spaces provided with each instruction.

Part 1. $^{36}Ar^+ + {}^{40}Ar \rightarrow {}^{36}Ar + {}^{40}Ar^+$

Note: After you find the tuning conditions that achieve ln $Y \simeq$ ln W (i.e., $[^{40}Ar^+] \simeq [^{36}Ar^+]_0 - [^{36}Ar^+]$), the same parameter settings (lens potentials, etc.) must be used for ln W measurements as are used for ln Y measurements.

Note: For instructions 1–7 below, maintain a constant difference of ca. 40 eV between the nominal Ion Source Potential (ISP) and the Q2 Rod Offset (Q2RO); i.e., ISP-Q2RO$\simeq$*40 eV*.

Warning: If your instrument can only achieve a nominal collision energy which is *less than* 40 eV (LAB), please indicate here your maximum achievable collision energy.

_____ eV (LAB)

If you *cannot* achieve 40 eV (LAB), then use your maximum achievable collision energy in lieu of 40 eV for all measurements in Part 1 and Part 2.

Initial Tuning:

1. PIBON/TGOFF: Set Q1 and Q3 at the mass peak position for $^{36}Ar^+$. Measure the ion intensity at the mass peak position ($\simeq[^{36}Ar^+]_0$).
2. Repeat 1., but with PIBOFF/TGOFF to measure the corresponding background intensity.
3. PIBON/TGON: Add sufficient Ar target gas so the ion intensity $[^{36}Ar^+]$ becomes ca. 0.5 $[^{36}Ar^+]_0$.
4. Repeat 3., but with PIBOFF/TGON to measure the corresponding background intensity.
5. PIBON/TGON: Set Q1 at the mass peak position for $^{36}Ar^+$ and Q3 at the mass peak position for $^{40}Ar^+$. Measure the ion intensity at the mass peak position for $^{40}Ar^+$ ($\simeq[^{40}Ar^+]$).
6. Vary all the ion-optical elements of your instrument (q_2, lens potentials, rod offsets, resolution and ΔM control, etc.) as necessary to maximize $[^{40}Ar^+]$ and to roughly approximate $[^{40}Ar^+] \simeq [^{36}Ar^+]_0 - [^{36}Ar^+]$.
7. Repeat 1–6 through as many iterations as necessary to achieve $[^{40}Ar^+] \simeq [^{36}Ar^+]_0 - [^{36}Ar^+]$.

Q2 Stopping Curve (cf. *Precaution 3*):

8. PIBON/TGOFF: Set Q1 and Q3 at the mass peak position for $^{40}Ar^+$. Measure $[^{40}Ar^+]_0$ as a function of the Q2 rod offset (Q2RO) to generate a Q2 stopping curve. Vary Q2RO over a range of potentials from ca. 10 eV below the nominal ion source potential to just above the nominal ion source potential where 99% of the projectile ions are stopped. For each Q2RO used, retune q_2 to q_{react}^{max} before measuring each $[^{40}Ar^+]_0$ for the corresponding Q2RO. Plot $[^{40}Ar^+]_0$ vs Q2RO.
9. If your Q2 stopping curve (energy distribution) doesn't approximate that of reference [12] (viz. a sharp cutoff), raise the Q1 rod offset closer to the ion source potential. Then repeat 1–7, as necessary, to ensure that the tuning of the ion-optical elements has maintained $[^{40}Ar^+] \simeq [^{36}Ar^+]_0 - [^{36}Ar^+]$. Then repeat 8 (and 9 if necessary).
10. For your final Q2 stopping curve, enter the values of $[^{40}Ar^+]_0$ vs the Q2 rod offset (Q2RO) in the spaces provided, and submit a hardcopy of the corresponding plot.

$[^{40}Ar^+]_0$	_____	_____	_____	_____	_____	_____	_____	_____
Q2R0, V	_____	_____	_____	_____	_____	_____	_____	_____
$[^{40}Ar^+]_0$	_____	_____	_____	_____	_____	_____	_____	_____
Q2R0, V	_____	_____	_____	_____	_____	_____	_____	____

$[^{40}Ar^+]_0$	_____	_____	_____	_____	_____	_____	_____	_____
Q2R0, V	_____	_____	_____	_____	_____	_____	_____	_____

Please submit a record of the settings of all your ion-optical elements (lenses, rod offsets, etc.) used to accomplish 10. Also, please submit a copy of a simplified schematic diagram (layout) showing the ion-optical components of your instrument from the ion source through the detector. Please label each ion-optical element so we can identify the settings with the schematic layout.

Note: Use the final Q2 stopping curve developed in instruction 10 to determine E_{50} (≡the Q2 rod offset that stops 50% of the projectile ions). For instructions 11–31 below, set the Q2 rod offset= (E_{50}−40) eV and set *all* the other ion-optical elements to the same values as were used for the final Q2 stopping curve of instruction 10.

Interference of $^{40}Ar^+$ at m/z 36 and of $^{36}Ar^+$ at m/z 40:

11. PIBON/TGOFF: Set Q1 at the mass peak position for $^{36}Ar^+$ and Q3 at the mass peak position for $^{36}Ar^+$ [*Precaution* 6 (i)]. Measure and record the intensity at the mass peak position for $^{36}Ar^+$. _____
12. Repeat 11, but with PIBOFF/TGOFF to measure the corresponding background intensity. _____
13. PIBON/TGOFF: Set Q1 at the mass peak position for $^{36}Ar^+$ and Q3 at the mass peak position for $^{40}Ar^+$. Measure and record the intensity at the mass peak position for $^{40}Ar^+$. _____
14. Repeat 13, but with PIBOFF/TGOFF to measure the corresponding background intensity. _____
15. PIBON/TGOFF: Set Q1 at the mass peak position for $^{40}Ar^+$ and Q3 at the mass peak position for $^{40}Ar^+$. Measure and record the intensity at the mass peak position for $^{40}Ar^+$. _____
16. Repeat 15, but with PIBOFF/TGOFF to measure the corresponding background intensity. _____
17. PIBON/TGOFF: Set Q1 at the mass peak position for $^{40}Ar^+$ and Q3 at the mass peak position for $^{36}Ar^+$. Measure and record the intensity at the mass peak position for $^{36}Ar^+$. _____
18. Repeat 17, but with PIBOFF/TGOFF to measure the corresponding background intensity. _____

ln Y and ln W Measurements:

All ln Y/ln W measurements within this Part 1 should be done at the same time (cf. *Precaution* 6). Record P/XQQ, ln Y, ln W, ARLEFF/LNY, and ARLEFF/LNW in the spaces provided. Please observe *Precaution* 8..

For $[^{36}Ar^+]/[^{36}Ar^+]_0 \simeq 0.5$:

19. PIBON/TGOFF: Set Q1 and Q3 at the mass peak position for $^{36}Ar^+$. Measure the ion intensity at the mass peak position ($\simeq[^{36}Ar^+]_0$). _____
20. Repeat 19, but with PIBOFF/TGOFF to measure the corresponding background intensity. _____
21. PIBON/TGON: Add sufficient Ar target gas so the ion intensity becomes $[^{36}Ar^+] \simeq 0.5\ [^{36}Ar^+]_0$. Measure the ion intensity at the mass peak position ($\simeq[^{36}Ar^+]$). _____
22. Repeat 21, but with PIBOFF/TGON to measure the corresponding background intensity. _____
23. PIBON/TGON: Set Q1 at the mass peak position for $^{36}Ar^+$ and Q3 at the mass peak position for $^{40}Ar^+$. Measure the ion intensity at the mass peak position for $^{40}Ar^+$ ($\simeq[^{40}Ar^+]$). _____

P/XQQ=_____ ln Y=_____ ln W=_____
ARLEFF/LNY=_____ ARLEFF/LNW=_____

24. Repeat 19–23, but with sufficient Ar target gas so that $[^{36}Ar^+]/[^{36}Ar^+]_0 \simeq 0.8$. Record your measurements in the spaces provided for the corresponding instructions.

"19."_____ "20."_____ "21."_____ "22."_____ "23."_____
P/XQQ=_____ ln Y=_____ ln W=_____
ARLEFF/LNY=_____ ARLEFF/LNW=_____

25. Repeat 19–23, but with sufficient Ar target gas so that $[^{36}Ar^+]/[^{36}Ar^+]_0 \simeq 0.6$. Record your measurements in the spaces provided for the corresponding instructions.

"19."_____ "20."_____ "21."_____ "22."_____ "23."_____
P/XQQ=_____ ln Y=_____ ln W=_____
ARLEFF/LNY=_____ ARLEFF/LNW=_____

26. Repeat 19–23, but with sufficient Ar target gas so that $[^{36}Ar^+]/[^{36}Ar^+]_0 \simeq 0.9$. Record your measurements in the spaces provided for the corresponding instructions.

"19."_____ "20."_____ "21."_____ "22."_____ "23."_____
P/XQQ=_____ ln Y=_____ ln W=_____
ARLEFF/LNY=_____ ARLEFF/LNW=_____

27. Repeat 19–23, but with sufficient Ar target gas so that $[^{36}Ar^+]/[^{36}Ar^+]_0 \simeq 0.7$. Record your measurements in the spaces provided for the corresponding instructions.

"19."_____ "20."_____ "21."_____ "22."_____ "23."_____
P/XQQ=_____ ln Y=_____ ln W=_____
ARLEFF/LNY=_____ ARLEFF/LNW=_____

28. Repeat 19–23 for $[^{36}Ar^+]/[^{36}Ar^+]_0 \simeq 0.5$:

"19."_____ "20."_____ "21."_____ "22."_____ "23."_____
P/XQQ=_____ ln Y=_____ ln W=_____
ARLEFF/LNY=_____ ARLEFF/LNW=_____

29. PIBON/TGOFF: Set Q1 and Q3 at the mass peak position for $^{36}Ar^+$. Measure the ion intensity at the mass peak position ($\simeq[^{36}Ar^+]_0$). _____
30. Repeat 29, but with PIBOFF/TGOFF to measure the corresponding background intensity. _____
31. Generate XQQCALPLOT by plotting ARLEFF/LNY vs P/XQQ and ARLEFF/LNW vs P/XQQ on the same graph. Submit a hardcopy of your XQQCALPLOT graph.

Note: If the two plots are not superimposable [i.e., same slope and intercept (to within ±10%)], your instrument HARDWARE does not have a dynamically-correct design (cf. reference [9]). Nonetheless, please proceed with Part 2 to assess other aspects of your instrument design.

Part 2. $N_2^+ + SF_6 \rightarrow N_2 + SF_5^+$

Note: In Part 2, you will be tuning you instrument to achieve $[SF_5^+] \simeq [N_2^+]_0 - [N_2^+]$. However, your detector may suffer significant differences in absolute response for SF_5^+ vs N_2^+ [i.e., the Conversion Gain CG_{127} for SF_5^+ (m/z 127) may differ substantially from the conversion gain CG_{28} for N_2^+ (m/z 28)]. You will, therefore, determine CG_{127}/CG_{28} at the end of Part 2. In the meantime, observe *Precaution* 6 (iv), and maximize $[SF_5^+]$ to approximate as best you can $[SF_5^+] \simeq [N_2^+]_0 - [N_2^+]$. For example, if $CG_{127}/CG_{28} \simeq 0.9$, you may find the best you can do is $[SF_5^+] \simeq 0.8\{[N_2^+]_0 - [N_2^+]\}$.

Note: Please observe *Precaution* 8. For the sensor you are using to make P/XQQ measurements, record here the type of sensor (Bayard-Alpert Ion Gauge, mass flowmeter, etc.) and its relative sensitivity (i.e., the response factor) for SF_6 relative to Ar.
Type of sensor_____ Response Factor (SF_6/Ar)_____

Note: For instructions 1–7 below, maintain a constant difference of ca. 40 eV between the nominal Ion Source Potential (ISP) and the Q2 Rod Offset (Q2RO); i.e., ISP-02RO≃40 eV.

Warning: If your instrument can only achieve a nominal collision energy which is *less than* 40 eV (LAB), then use your maximum achievable collision energy in lieu of 40 eV, as you did for Part 1.

Initial Tuning:

1. PIBON/TGOFF: Set Q1 and Q3 at the mass peak position for N_2^+ with $q_2 = q_{react}^{max}$. Measure the ion intensity at the mass peak position ($\simeq[N_2^+]_0$).
2. Repeat 1, but with PIBOFF/TGOFF to measure the corresponding background intensity.
3. PIBON/TGON: Add sufficient SF_6 target gas so the ion intensity $[N_2^+]$ becomes ca. 0.6 $[N_2^+]_0$.
4. Repeat 3, but with PIBOFF/TGON to measure the corresponding background intensity.
5. PIBON/TGON: Set Q1 at the mass peak position for N_2^+ and Q3 at the mass peak position for SF_5^+ (m/z 127). Measure the ion intensity at the mass peak position for SF_5^+ ($\simeq[SF_5^+]$).
6. Vary all the ion-optical elements of your instrument ($q_2 = q_{prod}^{max}$, lens potentials, rod offsets, resolution and ΔM control, etc.) as necessary to maximize $[SF_5^+]$ and to roughly approximate $[SF_5^+] \simeq [N_2^+]_0 - [N_2^+]$.
7. Repeat 1–6 through as many iterations as necessary to optimize $[SF_5^+] \simeq [N_2^+]_0 - [N_2^+]$.

Q2 Stopping Curve (cf. *Precaution* 3):

8. PIBON/TGOFF: Set Q1 and Q3 at the mass peak position for N_2^+. Measure $[N_2^+]_0$ as a function of the Q2 rod offset (Q2RO) to generate a Q2 stopping curve. Vary Q2RO over a range of potentials from ca. 10 eV below the nominal ion source potential to just above the nominal ion source potential where 99% of the projectile ions are stopped. For each Q2RO used, retune q_2 to q_{react}^{max} before measuring each $[N_2^+]_0$ for the corresponding Q2RO. Plot $[N_2^+]_0$ vs Q2RO.
9. If your Q2 stopping curve (energy distribution) doesn't approximate that of reference [14], raise the Q1 rod offset closer to the ion source potential. Then repeat 1–7, as necessary, to ensure that the tuning of the ion-optical elements has maintained $[SF_5^+] \simeq [N_2^+]_0 - [N_2^+]$. Then repeat 8 (and 9 if necessary).
10. For your final Q2 stopping curve, enter the values of $[N_2^+]_0$ vs the Q2 rod offset (Q2RO) in the spaces provided, and submit a hardcopy of the corresponding plot.

$[N_2^+]_0$	_____	_____	_____	_____	_____	_____	_____	_____
Q2R0, V	_____	_____	_____	_____	_____	_____	_____	_____
$[N_2^+]_0$	_____	_____	_____	_____	_____	_____	_____	_____
Q2R0, V	_____	_____	_____	_____	_____	_____	_____	_____
$[N_2^+]_0$	_____	_____	_____	_____	_____	_____	_____	_____
Q2R0, V	_____	_____	_____	_____	_____	_____	_____	_____

Please submit a record of the settings of all your ion-optical elements (lenses, rod offsets, etc.) used to accomplish 10.

Note: Use the final Q2 stopping curve developed in instruction 10 to determine E_{50} (≡the Q2 rod offset that stops 50% of the projectile ions). For instructions 11–39 below, set the Q2 rod offset= (E_{50}−40) eV and set *all* the other ion-optical elements to the same values as were used for the final Q2 stopping curve of instruction 10.

Ion Intensity vs q_2:

Note: The q_2 values (referenced to q_3) must be varied in small increments to ensure that the measurements made here represent correctly the ion imaging occurring within your Q2Q3 structure (i.e., there may be severe oscillations in the ion intensity as q_2 is varied). These data will be used to make the necessary corrections for differences in the relative reaction pathlength and in relative transmission (cf. reference [14]).

Note: For instructions 11–17, verify that Q1 and Q3 are still set at their respective mass peak positions each time a different q_2 value is selected.

11. PIBON/TGOFF: Set Q1 and Q3 at the mass peak position for N_2^+. Measure the ion intensity at the mass peak position ($\simeq[N_2^+]_0$) as a function of q_2. Use values of q_2 between ca. 0.1 and 0.7. Record your measurements in the spaces provided.

$[N_2^+]_0$								
q_2								
$[N_2^+]_0$								
q_2								
$[N_2^+]_0$								
q_2								

12. PIBOFF/TGOFF: Measure the corresponding background intensity at just one value of q_2. _____
13. PIBON/TGON: Add sufficient SF_6 target gas so the ion intensity $[N_2^+]$ becomes ca. 0.7 $[N_2^+]_0$. Measure the ion intensity at the mass peak position for N_2^+($\simeq[N_2^+]$) as a function of q_2. Use values of q_2 between ca. 0.1 and 0.7. Record your measurements in the spaces provided.

$[N_2^+]$								
q_2								
$[N_2^+]$								
q_2								
$[N_2^+]$								
q_2								

14. PIBOFF/TGON: Measure the corresponding background intensity at just one value of q_2. _____
15. PIBON/TGON: Set Q1 at the mass peak position for N_2^+ and Q3 at the mass peak position for SF_5^+. Measure the ion intensity at the mass peak position for SF_5^+ ($\simeq[SF_5^+]$) as a function of q_2. Use values of q_2 between ca. 0.1 and 0.7. Record your measurements in the spaces provided.

$[SF_5^+]$								
q_2								
$[SF_5^+]$								
q_2								
$[SF_5^+]$								
q_2								

16. PIBOFF/TGON: Measure the corresponding background intensity at just one value of q_2. _____
17. Submit the data and hardcopy plots for $[N_2^+]_0$ vs q_2, $[N_2^+]$ vs q_2, and $[SF_5^+]$ vs q_2.

ln *Y* and ln *W* Measurements:

Note: After you have found the tuning conditions that maximize SF_5^+ so that $[SF_5^+]\simeq[N_2^+]_0-[N_2^+]$, the same parameter settings (lens potentials, etc.) must be used for ln *W* measurements as are used for ln *Y* measurements. Only q_2 should be varied to tune to q_{react}^{max} for ion intensity measurements of N_2^+ and to q_{prod}^{max} for ion intensity measurements of SF_5^+.

All ln *Y*/ln *W* measurements within Part 2 should be done at the same time (cf. *Precaution* 6.). Record P/XQQ, and the other requisite measurements in the spaces provided. Please observe *Precaution* 8.

For $[N_2^+]/[N_2^+]_0 \simeq 0.6$:

18. PIBON/TGOFF: Set Q1 and Q3 at the mass peak position for N_2^+ with $q_2 = q_{react}^{max}$. Measure the ion intensity at the mass peak position ($\simeq[N_2^+]_0$). _____
19. Repeat 18, but with PIBOFF/TGOFF to measure the corresponding background intensity. _____
20. PIBON/TGON: Add sufficient SF_6 target gas so the ion intensity becomes $[N_2^+] \simeq 0.6\ [N_2^+]_0$. Measure the ion intensity at the mass peak position ($\simeq[N_2^+]$)._____ P/XQQ=_____.
21. Repeat 20, but with PIBOFF/TGON to measure the corresponding background intensity. _____
22. PIBON/TGON: Set Q1 at the mass peak position for N_2^+ and Q3 at the mass peak position for SF_5^+ with $q_2 = q_{prod}^{max}$. Measure the ion intensity at the mass peak position for SF_5^+ ($\simeq[SF_5^+]$). _____
23. Repeat 22, but with PIBOFF/TGON to measure the corresponding background intensity. _____
24. Repeat 18–23, but with sufficient SF_6 target gas so that $[N_2^+]/[N_2^+]_0 \simeq 0.8$. Record your measurements in the spaces provided for the corresponding instructions.

    "18."_____ "19."_____ "20."_____ "21."_____ "22."_____ "23."_____
    P/XQQ=_____

25. Repeat 18–23, but with sufficient SF_6 target gas so that $[N_2^+]/[N_2^+]_0 \simeq 0.7$. Record your measurements in the spaces provided for the corresponding instructions.

    "18."_____ "19."_____ "20."_____ "21."_____ "22."_____ "23."_____
    P/XQQ=_____

26. Repeat 18–23, but with sufficient SF_6 target gas so that $[N_2^+]/[N_2^+]_0 \simeq 0.9$. Record your measurements in the spaces provided for the corresponding instructions.

    "18."_____ "19."_____ "20."_____ "21."_____ "22."_____ "23."_____
    P/XQQ=_____

27. Repeat 18–23, but with sufficient SF_6 target gas so that $[N_2^+]/[N_2^+]_0 \simeq 0.6$. Record your measurements in the spaces provided for the corresponding instructions.

    "18."_____ "19."_____ "20."_____ "21."_____ "22."_____ "23."_____
    P/XQQ=_____

28. Repeat 20. _____ and 21. _____
29. Repeat 18. _____ and 19. _____

Detector's Conversion Gain Measurement:

You must make conversion gain measurements if your instrument uses analog current measurements. If your instrument uses *true* ion pulse counting (e.g., SCIEX TAGA 6000), conversion gain measurements are *not* needed [i.e., ignore this section (instructions 30–39)].

Warning: Some instruments use analog current measurements, but report the ion intensities as ion count rates within their data systems (i.e., the ion currents are converted to equivalent ion count rates via current-to-frequency converters or voltage-to-frequency converters or ?). Such instruments still require conversion gain measurements.

Here you will determine the ratio CG_{127}/CG_{28} for the conversion gain of SF_5^+ relative to that of N_2^+. However, to avoid complicating the conversion gain measurements, do not use SF_5^+. Instead, use n-butylbenzene (m/z 134) or other stable compound with a mass close to 127.

30. In general, follow the manufacturer's recommendations for conversion gain measurements. However, if your detector uses a conversion dynode, please observe the following additional precautions to ensure reproducible results.

Note: When making absolute current measurements with the detector turned on, use all the settings used for instructions 18–29. When you are using the Faraday cup (for absolute ion current measurements), turn off the detector's high voltage but use all the other settings used for instructions 18–29.

31. Make sure both the N_2 and the n-butylbenzene are flowing together into the ion source at all times. Use a fixed flow rate. Do 32–39 after the flows have stabilized (constant pressure in the ion source region).
32. PIBON/TGOFF: Set Q1 and Q3 at the mass peak position for N_2^+ with $q_2 = q_{react}^{max}$ for m/z 28. Leave everything turned on and monitor $[N_2^+]_0$ until it reaches the final (highest or lowest) stabilized ion current for $[N_2^+]_0$ (ca. 10–15 minutes).
33. PIBON/TGOFF: Set Q1 and Q3 at the mass peak position for 134^+ with $q_2 = q_{react}^{max}$ for m/z 134. Immediately record the initial absolute current measured for $[134^+]$ with the detector turned on.

    $I_{detector}$=_____ for m/z 134.

34. Repeat 32.
35. PIBON/TGOFF: Set Q1 and Q3 at the mass peak position for 134^+ with $q_2 = q_{react}^{max}$ for m/z 134. Immediately record the initial absolute current measured for $[134^+]$ with the Faraday cup.

    $I_{Faraday}$=_____ for m/z 134.

36. The ratio of $I_{detector}/I_{Faraday}$ from 33 and 35 provides an estimate for CG_{134}=_____.
37. Repeat 32–36, but use m/z 28 instead of m/z 134 in 33 and 35. For m/z 28, $I_{detector}$=_____ $I_{Faraday}$=_____ CG_{28}=_____
38. The values from 36 and 37 provide an estimate for the ratio CG_{134}/CG_{28}=_____.
39. Repeat 32–38 at least one more time to ensure your estimates for CG_{127}, CG_{28}, and CG_{127}/CG_{28} are reproducible.

Conclusion:

40. For each XQQ instrument, please submit:
    (1) this completed test protocol (i.e., with the blank spaces filled in)
    (2) a copy of the completed *Questionnaire*
    (3) any other data requested herein.
    Thank you.

Questionnaire

Note: Put a large asterisk (*) next to any proprietary (confidential) information which must not be divulged.

Participant's Name and Address: _____
_____
_____
_____
_____
Phone: _____

What type of XQQ instrument (QQ, QQQ, BEQQ, etc.)? _____
Manufacturer? _____ Model No.? _____
Does your XQQ instrument use a molecular beam target within Q2 (e.g., SCIEX TAGA 6000) or a collision cell enclosure surrounding Q2 (e.g., Finnigan TSQ70)?
Check one: Molecular beam _____ Collision enclosure _____
If a collision cell enclosure surrounds Q2, what is the rectilinear pathlength of the collision region (from the entrance aperture to the exit aperture)? _____cm

Quadrupole Rod Assemblies:

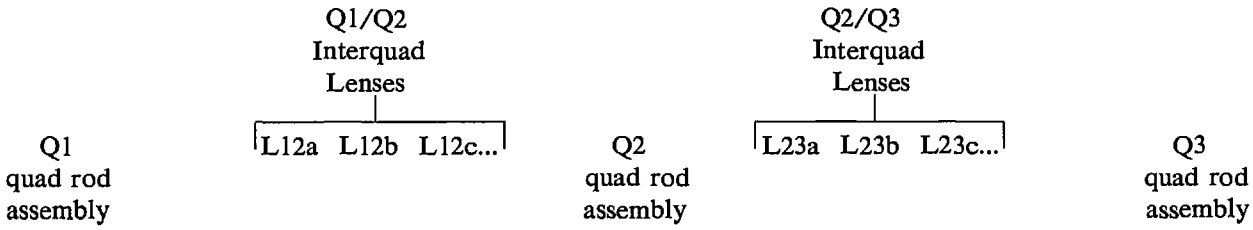
Is the Q1 quad rod assembly enclosed within a housing (enclosure) or uncovered (nude rods, no housing) within the vacuum chamber? Enclosed _____ Uncovered _____
Is the Q3 quad rod assembly enclosed within a housing (enclosure) or uncovered (nude rods, no housing) within the vacuum chamber? Enclosed _____ Uncovered _____
What is the rectilinear length of the Q2 quad rod assembly? _____cm
What is the field radius r_0 for the Q2 quad rod assembly? _____cm
If cylindrical rods are used for the Q2 quad rod assembly, what is the rod diameter? _____cm
Does each quad rod assembly (Q1, Q2, Q3) have its own separate rf/dc generator (quadrupole controller/power supply)? Yes _____ No _____
If you answered "No", which ones don't? Q1 _____ Q2 _____ Q3 _____
What is the frequency of operation for Q2? _____MHz
- (if variable frequencies are used for Q2, what nominal frequency was used for Ar^+? _____MHz for N_2^+? _____MHz for SF_5^+? _____MHz)

What is the frequency of operation for Q1? _____MHz
- (if variable frequencies are used for Q1, what nominal frequency was used for Ar^+? _____MHz for N_2^+? _____MHz for SF_5^+? _____MHz)

What is the frequency of operation for Q3? _____MHz
- (if variable frequencies are used for Q3, what nominal frequency was used for Ar^+? _____MHz for N_2^+? _____MHz for SF_5^+? _____MHz)

Interquadrupole Lenses:

Answer the questions below with reference to the following simplified schematic:



How many lenses are there betwen the Q1 quad rod assembly and the Q2 quad rod assembly (include the Q1 exit aperture and the Q2 entrance aperture in your count)? _____

What is the nominal diameter (in cm) of the aperture of each of the L12 interquadrupole lenses? L12a _____ L12b _____ L12c _____ L12d _____ L12e _____

If you are using a hybrid XQQ instrument (e.g., BEQQ, etc.), indicate the diameter (in cm) of the Q2 entrance aperture _____.

How many lenses are there between the Q2 quad rod assembly and the Q3 quad rod assembly (include the Q2 exit aperture and the Q3 entrance aperture in your count)? _____

What is the diameter (in cm) of the aperture of each of the L23 interquadrupole lenses? L23a _____ L23b _____ L23c _____ L23d _____ L23e _____

Modes of Operation:

Parent-scan mode: Q3 is set to a fixed mass while Q1 scans over a range of masses; one can thus assess which parent ion masses are the progenitors of a given daughter ion mass.

Daughter-scan mode: Q1 is set to a fixed mass while Q3 scans over a range of masses; one can thus assess which daughter ion masses are the progeny of a given parent ion mass.

For the parent-scan mode, how is the value of q_2 set in your instrument?

Check all that apply: It can be referenced to q_1? _____
It can be referenced to q_3? _____
Other? (Explain) _____
_____

For the daughter-scan mode, how is the value of q_2 set in your instrument?

Check all that apply: It can be referenced to q_1? _____
It can be referenced to q_3? _____
Other? (Explain) _____
_____

Comments:

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